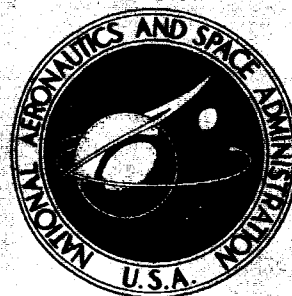


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SYNTHESIS OF PHOSPHONIC POLYESTERS BY TRANSESTERIFICATION

by Samuel Kohn

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SYNTHESIS OF PHOSPHONIC POLYESTERS
BY TRANSESTERIFICATION

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Samuel Kohn*

ABSTRACT

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The results of experiments in the preparation of phosphonic polyesters by three methods of transesterification (alcoholysis, acidolysis, and true transesterification) are presented following a survey of the pros and cons of the various syntheses of phosphonic polyesters. Acidolysis is the simplest technique for the preparation of polyphosphonates, but polyphosphonates of a diphenol can be prepared by the alcoholysis of a diphenyl phosphonate. It is also shown that true transesterification never occurs. When it appears to take place, what actually occurs is acidolysis by the free phosphonic acid formed by thermal destruction of the ethyl phosphonate used to initiate the reaction.

I. INTRODUCTION

Author

The problem of synthesizing thermostable polymers which are simultaneously tough and chemically inert is the prime objective of modern macromolecular research. In view of the difficulty of solving the problem with macromolecules comprised solely of carbon, hydrogen, and oxygen atoms, polymers containing nitrogen, silicon, and fluorine have become increasingly manifest. These polymers have provided their users with at least partial satisfaction. They are distinguished above all by enhanced thermal stability and a high chemical inertness.

*With the technical assistance of R. Ramain and M. D. Charrier.

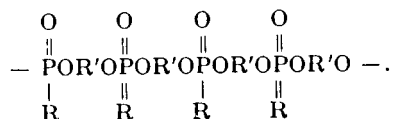
**Numbers in the margin indicate pagination in the original foreign text.

But these products have rapidly proven themselves inadequate, and research is being aimed more toward other organomineral or mineral structures. Compounds of phosphorus, boron, germanium, titanium, aluminum, etc. have been added to the realm of macromolecular chemistry. The organophosphoric derivatives hold particularly high esteem among specialists, a status that is well justified.

In fact, whereas the binding energy of the phosphorus-carbon bond is almost equivalent to that of the carbon-carbon bond, the simple phosphorus-oxygen bond exceeds the carbon-oxygen bond by 10 kcal/mole and the double phosphorus-oxygen bond (113 to 140 kcal/mole) exceeds the carbon-oxygen bond ($C=O$) by 55 kcal/mole.

Moreover, the phosphorus atoms are distinguished by a large chemical reactivity of the nucleophilic type. The well known attributes of thermal stability, noninflammability, occasionally noncombustibility, inertness with respect to numerous chemical agents are additional virtues of the phosphorus derivatives.

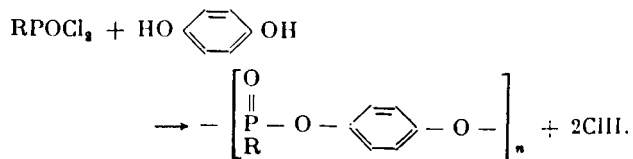
The polyphosphonates comprise one example of polymers with an organomineral skeleton:



II. PHOSPHONIC POLYESTERS

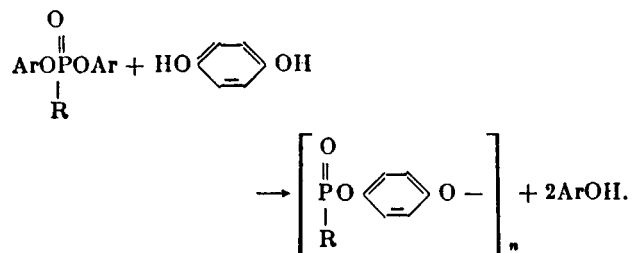
The synthesis of phosphonic polyesters has been performed by the following methods:

1) Action of the chlorides of phosphonic acids on the diphenols or glycols in the presence of tin, zinc, or magnesium chloride (ref. 1):

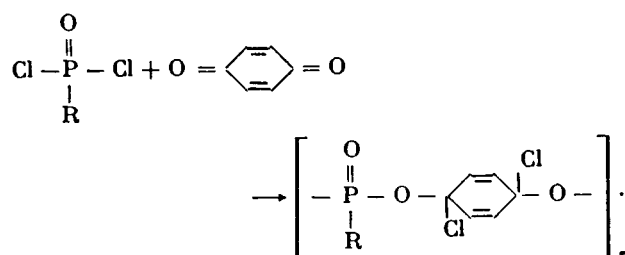


2) Phenolysis of a phosphonic ester (ref. 2):

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3) Action of an acid chloride on a quinone (ref. 3):



It is interesting to note that the conventional method of synthesis of carboxylic polyesters, consisting in the action of a diacid on a diol, cannot be used in the case of the organophosphoric compounds. The presence of a phosphorus atom in the molecule diminishes the reactivity of the free hydroxyl groups contained in the monoester molecule, and a single hydroxyl can be esterified (ref. 1). It is impossible, therefore, to obtain a phosphonic polyester by this means.

The methods described have the further disadvantage of rendering some polymers rather poorly defined and variable, depending on the particular author and manner of operation.

The reaction of acid chlorides on diols is violent and unamenable to control. It is difficult to use this method if one wishes to carry out the synthesis in large quantities. It is more easily realized in solution, but the

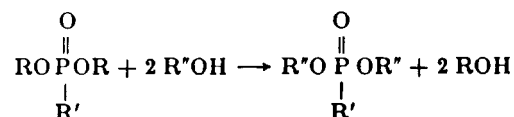
presence of solvents is an extreme disadvantage; the complete elimination of the solvent is very tedious and costly, besides which it is difficult to obtain a polymer of high molecular weight.

Preparation of the polyester by alcoholysis would be more interesting, were it not for the disadvantage, as we will see presently, that it is accompanied by secondary reactions in the case of the aliphatic diols.

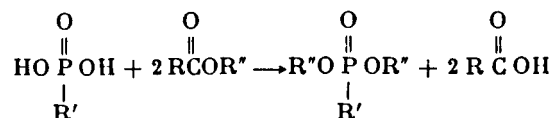
The importance of finding a synthesis based on transesterification without concomitant secondary reactions has motivated us to pursue this line of research.

The term transesterification usually encompasses three rather distinct reactions:

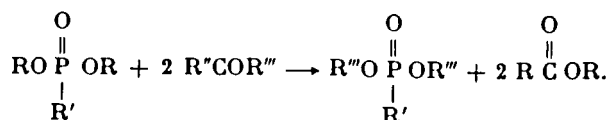
1) The replacement of an alcohol in an ester by another alcohol, i.e., alcoholysis:



2) The replacement of an acid in an ester by another acid, i.e., acidolysis:



3) So-called true transesterification, or the exchange of alcohols between two esters:



The three modes of esterification have been systematically investigated, the results being summarized in the present work.

III. EXPERIMENTAL TECHNIQUES

The various experiments with alcoholysis, acidolysis, and transesterification were carried out under the following conditions:

III.1. Apparatus

The apparatus consisted of a round bottom flask from 50 to 100 cm³ capacity, equipped with a tube for the inflow of nitrogen just below the surface of the liquid (this tube position prevents the excessive entrainment of vapors from the investigated product) and another tube intended for collection the volatile products.

This tube has a bulb that serves as an ambient temperature trap; it is followed by two more traps, which are successively cooled by ice water and liquid nitrogen. After the third trap is a round bottom flask serving as a nitrogen reserve (fig. 1), in order to prevent any ingress of air during the reaction.

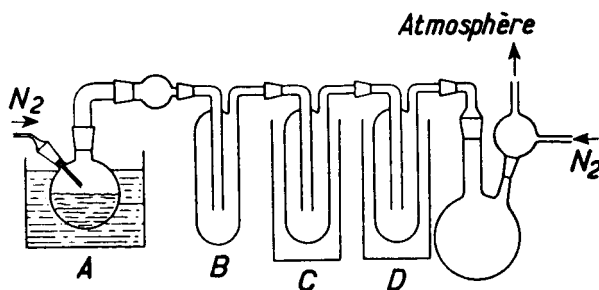


Figure 1. Apparatus Used for Transesterification.

A) Salt Bath; B) Ambient; C) Icewater; D) Liquid Nitrogen

In the case of transesterification at 300°C, the first tube was encased in a straight tube rising high enough to ensure reflux of the most volatile reagents.

III.2. Procedure

1/10 mole of the reagent to be studied was placed in the round bottom reaction flask, in which 1/1000 mole of anhydrous magnesium chloride was added. The flask, connected to the various traps and subjected to prior evacuation of all traces of air by prolonged bubbling with residual nitrogen, was immersed in 21 a thermostat, which was regulated within $\pm 2^\circ$ of the desired temperature.

The duration of the reaction was set arbitrarily at 6 hr.

At the conclusion of each operation, the contents of the traps were examined with an infrared spectrograph, following the customary procedure. In particular, the solid products were investigated in pellet form in a mixture with potassium bromide.

III.3. Alcoholysis

The tests described in this section have already been discussed in a report to the Academy of Sciences (ref. 4), so that we will confine ourselves to a brief exposition.

The alcoholysis of phosphonic esters is not an easy matter, as it requires an elevated temperature and the presence of a catalyst. All of the alcoholysis experiments were carried out at 200°C . Four types of alcoholysis were studied:

- 1) aliphatic diol in ethyl butanephosphonate;
- 2) hydroquinone in ethyl butanephosphonate;
- 3) aliphatic diol in phenyl butanephosphonate;
- 4) hydroquinone in phenyl butanephosphonate.

An identical series of tests was carried out with the corresponding derivatives of benzenephosphonic acid.

Results: Phenyl butanephosphonate, like phenyl benzenephosphonate, yields with hydroquinone the exchange reaction described by Coover and McCall. Only

phenol is collected, and the product of the reaction is a polyphosphonate of hydroquinone. The polyphosphonate appears in the form of a sticky, more or less viscous brown solid. This alcoholysis is effected without secondary reaction.

By contrast, the diethyl phosphonates in the presence of hydroquinone lead to secondary products. In addition to the ethyl alcohol liberated by the exchange reaction, 1,4-diethoxybenzene, ethyl ether, water, and traces of ethylene are obtained; the presence of phosphonic acid is observed in the residue.

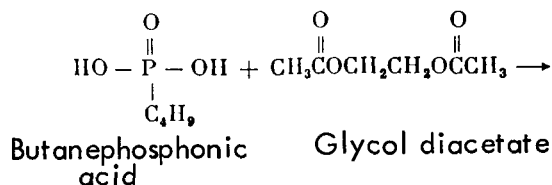
These compounds arise from the etherification reaction and the reaction of thermal degradation of the aliphatic phosphonate.

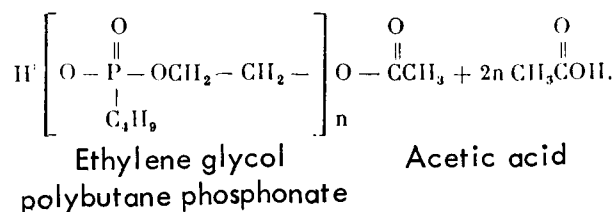
If the hydroquinone is replaced by an aliphatic diol, etherification becomes the principal reaction. For example, with butylene glycol, principally tetrahydrofuran is obtained. A portion of the glycol reacts as part of the exchange reaction, the latter being more accentuated in the case of the phenyl phosphonates. The esters thus obtained contain a high proportion of acids.

III.4. Acidolysis

Four tests were performed. In the first two, butanephosphonic acid was caused to act in succession on glycol diacetate and on hydroquinone diacetate; in the other two tests, benzenephosphonic acid was caused to act on the same diacetates.

The acidolysis reaction takes place according to the following scheme, which relates to the action of butanephosphonic acid on glycol diacetate:





All of these reactions lead, at least theoretically, to the formation of a glycol polyphosphonate or hydroquinone of acetic acid. The presence of this volatile acid in the traps is a clear indication that the desired reaction has taken place.

In every case, the residue appears in the form of a very viscous paste, going over to a solid only in the case of the hydroquinone polybutanephosphonate.

The results of these tests are summarized in table I.

The acidolysis reaction in the presence of magnesium chloride occurs in the four cases at 200°C much more readily than alcoholysis. It is more complete for the hydroquinone acetate than for the glycol acetate. This phenomenon may be attributed to the difference in volatility of the initial products. We will elaborate on this issue during the discussion of transesterification.

We were unable to find any trace of the products of degradation capable of proceeding from the decomposition of one of the reagents present during the course of the reaction of the phosphonic acids to the glycol acetate. On the contrary, during the reactions of the two acids with the hydroquinone diacetate, traces of an unidentifiable gas were produced in the liquid nitrogen trap.

IV. TRANSESTERIFICATION

Two series of tests were carried out, one at 200° and the other at 300°C. In each series we used:

- two esters of butanephosphonic acid (diethyl ester and diphenyl ester);
- two esters of benzenephosphonic acid (diethyl ester and diphenyl ester).

TABLE I

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ACIDOLYSIS AT 200°C

Initial products		Reaction products			
Phosphonic acid	Carboxylic ester	Ambient trap	Icewater trap	Liquid nitrogen trap	Residue
Butanephosphonic acid	glycol acetate	acetic acid	-	-	brown liquid with small amount of glycol acetate; no more OH acids
Butanephosphonic acid	hydroquinone acetate	acetic acid	acetic acid	trace of unidentified gas	solid polymer
Benzenephosphonic acid	glycol acetate	acetic acid	-	-	viscous liquid; incomplete reaction, polymer contains phosphonic acid
Benzenephosphonic acid	hydroquinone acetate	acetic acid	-	trace of unidentified gas	black solid containing hydroquinone acetate and traces of benzenephosphonic acid

Exchange had to occur respectively between each of these esters and two diacetates, one aliphatic (glycol diacetate) and the other aromatic (hydroquinone diacetate). The tests at 300° were preceded by an examination of the behavior of each reagent used at this temperature, heated in the presence of magnesium chloride.

The results of the tests at 200°C are found in table II, the results of the examination of the reagents at 300° in table III, and the results of the transesterification tests at 300° in table IV. The various experimental results are discussed in the ensuing pages.

TABLE II

TRANSESTERIFICATION AT 200°C

Initial products		Reaction products				Observations
Phosphonic ester	Carboxylic ester	Ambient trap	Icewater trap	Liquid nitrogen trap	Residue	
ethyl butane-phosphonate	glycol acetate	-	-	-	product unaltered	no reaction
"	hydroquinone acetate	-	small amount of ethyl acetate; traces of acetic acid and ethyl alcohol	ethylene, propylene, ethyl acetate	liquid containing small amount of hydroquinone phosphate mixed with acetic acid and ethyl butane-phosphonate	incipient reaction
ethyl benzene-phosphonate	glycol acetate	-	traces of ethyl alcohol, acetic acid, and water	ethyl acetate	product unaltered	no reaction
"	hydroquinone acetate	-	small amount of ethyl acetate; traces of acetic acid	ethylene	paste containing crystals; slight modification; increased content of benzene nuclei	incipient reaction
phenyl butane-phosphonate	glycol acetate	-	-	-	product unaltered	no reaction
"	hydroquinone acetate	-	-	-	product unaltered	no reaction

TABLE II (Cont.)

Initial products		Reaction products				Observations
Phosphonic ester	Carboxylic ester	Ambient trap	Icewater trap	Liquid Nitrogen trap	Residue	
phenyl benzene-phosphonate	glycol acetate	-	-	-	product unaltered	no reaction
"	hydroquinone acetate	-	-	-	slight modification	incipient reaction

TABLE III

EFFECT OF HEAT ON THE INITIAL REAGENTS

Reagent	Ambient trap	Icewater trap	Liquid nitrogen trap	Residue	Observations
glycol acetate	glycol acetate	-	-	product unaltered	no reaction
hydroquinone acetate	traces of hydroquinone acetate	-	-	product unaltered except for liquid coloration	no reaction
ethyl butane-phosphonate	-	-	traces of ethylene	product unaltered, yellow coloration of liquid	no reaction
phenyl butane-phosphonate	traces of phenol	-	-	product unaltered, liquid coloration	no reaction
ethyl benzene-phosphonate	benzene and traces of ethyl alcohol	traces of ethyl alcohol and water	ethylene in significant amount	two layers, one liquid, the other paste; liquid layer composed of benzene; paste of benzenephosphonic acid	reaction of very advanced decomposition
phenyl benzene-phosphonate	-	-	-	product unaltered	no reaction

TABLE IV

TRANSESTERIFICATION AT 300°C

Initial products		Reaction products				
Phosphonic ester	Carboxylic ester	Ambient trap	Icewater trap	Liquid nitrogen trap	Residue	Observations
Ethyl butane-phosphonate	glycol acetate	glycol acetate	-	-	product unaltered	no reaction
"	hydroquinone acetate	ethyl acetate	ethyl acetate; small quantities of alcohol and acetic acid	ethylene, CO ₂ , CO	hydroquinone butanephosphonate; brown resin soln. in benzene. Softens near 120°C	very advanced reaction
ethyl benzene-phosphonate	glycol acetate	-	water; acetic acid; ethyl alcohol	ethylene, glycol acetate, alcohol	product unaltered	no reaction
"	hydroquinone acetate	ethyl acetate	ethyl acetate; traces of acetic acid	ethylene, CO ₂	porous brown solid; hydroquinone benzene-phosphonate, appears to have undergone incipient decomposition; no sign of acetate	almost complete reaction
phenyl butane-phosphonate	glycol acetate	-	acetic acid; small amount of acetic anhydride	small amounts of gas and acids	product unaltered	no reaction
"	hydroquinone acetate	-	acetic acid and anhydride	small amounts of gas, acids	product unaltered	no reaction

TABLE IV (Cont.)

TABLE IV (Cont.)						
Initial products		Reaction products				
Phosphonic ester	Carboxylic ester	Ambient trap	Icewater trap	Liquid nitrogen trap	Residue	Observations
phenyl benzene-phosphonate	glycol acetate	-	-	-	product unaltered	no reaction
"	hydroquinone acetate	traces of acetic acid and acetic anhydride	-	-	product unaltered	no reaction

IV.1. Transesterification at 200°C

An examination of table II reveals the onset of transesterification in the case of reaction between the diethyl esters of the two phosphonic acids and the hydroquinone acetate. Also noted is the presence of traces of volatile products in the traps in the case of reaction between ethyl benzenephosphonate and glycol acetate. These three reactions will be analyzed in succession below. /24

IV.1.1. Ethyl butanephosphonate and hydroquinone acetate. - The presence of ethyl acetate in the icewater trap indicates the onset of a reaction. We note, at the same time, the presence of products of degradation of the ethyl butanephosphonate, ethylene in the liquid nitrogen trap, ethyl alcohol and acetic acid in the icewater trap.

An infrared spectographic investigation of the liquid residue gives equal evidence to the onset of transesterification. In fact, the presence of hydroquinone butanephosphonate fairly well confirms this.

IV.1.2. Ethyl benzenephosphonate and hydroquinone acetate. - In this case, we also find ethyl acetate, ethyl alcohol, and acetic acid in the icewater trap, as well as ethylene in the liquid nitrogen trap. According to infrared spectral analysis, the residue is rich in benzene nuclei, which would tend to indicate the formation of hydroquinone benzenephosphonate.

IV.1.3. Ethyl benzenephosphonate and glycol acetate. - There is no sign of transesterification in this case; the residue of the reaction remaining unaltered, one can attribute the presence of traces of ethyl alcohol, water, and acetic acid in the icewater trap and ethylene in the liquid nitrogen trap to degradation of the ethyl benzenephosphonate.

In summary, it may be asserted that at 200°C there is an incipient transesterification reaction, further accompanied by a certain degradation of the

phosphonic esters in the case when the diethyl esters of the two phosphonic acids are caused to act on the hydroquinone acetate.

The reaction is very advanced in the case of ethyl benzenephosphonate.

In the case of ethyl benzene phosphonate acting on glycol acetate, there is no transesterification, just decomposition of the ethyl benzenephosphonate.

IV.1.4. Stability of the investigated reagents at 300°C. - The various reagents were heated to 300°C over a period of four hours in the presence of 1/100 mole magnesium chloride under conditions identical to those of the transesterification experiments. Examination of table III, which presents the results of these tests, leads to the following assertions:

- Glycol acetate is not subject to decomposition.
- Hydroquinone acetate turns brown and is easily sublimated.
- Ethyl butanephosphonate is not subject to appreciable decomposition, although traces of ethylene are evident in the liquid nitrogen trap.
- Phenyl butanephosphonate remains practically unaffected, although its color turns brown.
- Ethyl benzenephosphonate undergoes rather intense decomposition. The presence of alcohol is evident in the icewater trap, and a significant amount of ethylene is present in the liquid nitrogen trap. The residue is made up of two layers, an upper colorless liquid layer of benzene and a lower solid brown layer of benzenephosphonic acid.

It is also apparent that in the case of transesterification such an intense decomposition does not take place. Phenyl benzenephosphonate remains essentially unchanged; nevertheless, there are traces of phenol in the ambient temperature trap.

Conclusion: The two ethyl phosphonates undergo decomposition after heating for four hours at 300°C. The ethyl benzenephosphonate undergoes a significant degradation, whereas the ethyl butanephosphonate only just begins to decompose under the same conditions.

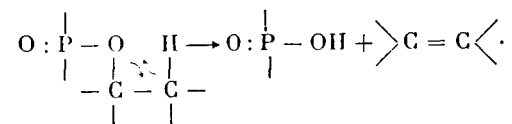
IV.2. Transesterification at 300°C

As suggested by the results of transesterification at 200°C, only the exchange reactions between the ethyl esters of the two phosphonic acids and the hydroquinone acetate lead to a significant yield of ethyl acetate and polyphosphonates of hydroquinone (see table IV).

These reactions are accompanied by secondary effects, including the formation of ethylene, carbon dioxide, carbon monoxide, ethyl alcohol, acetic acid and acetic anhydride.

In all other cases, as shown in table IV, there is no reaction between esters; only the presence of products of the decomposition of the initial reagents is observed in the traps. The presence of ethylene and acetic acid can be explained as follows:

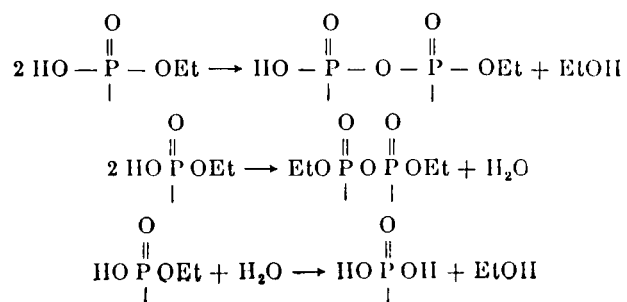
On decomposing, the ethyl phosphonates yield ethylene phosphonic acid. According to Canavan, Dowden, and Eaborn (ref. 5), this decomposition proceeds according to the following mechanism:



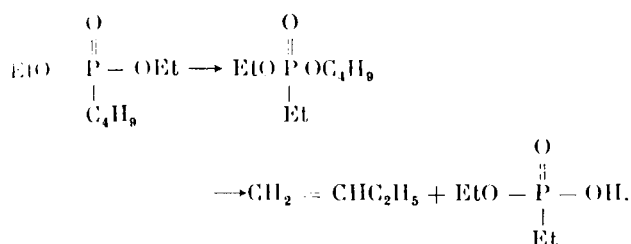
This represents an elimination of the β cis position, the generally accepted rule for explaining the decomposition of polyesters having their hydrogen atoms attached to a carbon atom situated in the β position of the carboxyl (ref. 6).

The phosphonic acid thus formed decomposes the acetate by acidolysis, forming a phosphonate or polyphosphonate of acetic acid.

Canavan and his co-workers explain the formation of ethyl alcohol and water by the following mechanism:



and, ultimately, the debutylation of the phosphonic acid in terms of the following mechanism: /25



The formation of acetic anhydride might be attributed to dehydration of the acetic acid in the presence of a more or less condensed phosphonate. In fact, such a phosphonate contains an anhydride function which can be transformed into a phosphonic acid, depending on the water supplied to the acetic acid (see the scheme of Canavan and co-workers).

The traces of CO_2 are probably formed by very weak decarboxylation of the acetic acid at this temperature.

CO was found in traces and its presence should be verified.

. The mechanism of transesterification can be explained by the following considerations:

Examination of tables II and IV, especially the latter, leads to the assumption that transesterification does not occur with appreciable intensity except in the case of the ethyl phosphonates acting on hydroquinone acetate. There is also an incipient esterification if ethyl benzenephosphonate is allowed to act on butanediol diacetate. In the case of ethyl butanephosphonate acting on butanediol diacetate, the reaction is considerably less advanced.

In every case, however, we detect the presence of ethylene, so that there occurs a decomposition resulting in the formation of a free phosphonic acid. Supplementary experiments were run, furnishing additional arguments in favor of this postulate.

1. Benzenephosphonic acid was allowed to act on ethyl benzenephosphonate at 300°C for six hours. A mixture containing 28% by weight of ethyl alcohol and 72% benzene was recovered in the icewater trap and ethylene in the liquid nitrogen trap, as products of the reaction.

Heated under the same conditions, the ethyl benzenephosphonate yielded only traces of ethyl alcohol. The presence of free phosphonic acid clearly promotes the formation of phosphonic acid from its ethyl ester.

2. Six millimoles of acetic acid were allowed to act on 50 millimoles of ethyl butanephosphonate for six hours. The result of this reaction was the formation of equal amounts by weight of alcohol and ethyl alcohol. The acidity of the residue was very slightly higher than that of the initial mixture. But ethyl butanephosphonate does not decompose even at 300°C (table III). This experiment proves that even the presence of a carboxylic acid leads to the formation of free phosphonic acid, beginning with its ethyl ester.

In the course of the transesterification experiments, we were never able to claim a true esterification reaction; on the contrary, every time that acidolysis was possible a reaction occurred. But in order for acidolysis to take place it is necessary to have the formation of free phosphonic acid.

Free phosphonic acids could not form except from their ethyl esters and there would not be a reaction except in the case of these esters.

This reaction was always accompanied by a more or less intense production of ethylene and ethyl alcohol. Moreover, the presence of a free acid augments the rate of formation of the phosphonic acids from their ethyl esters.

In the case of the phenyl phosphonates, which were stable at the experimental temperatures, it was not possible to detect the slightest exchange reaction. The formation of ethyl acetate in the case of the reaction of ethyl butanephosphonate with hydroquinone acetate can be explained by a mechanism other than transesterification. 126

In fact, we have earlier witnessed how the ethyl alcohol could be formed; this ethyl alcohol in the presence of acetic acid is transformed into ethyl acetate. The latter hypothesis is supported by the presence of alcohol and acetic acid in the traps.

Another question presents itself. Why is there a reaction when the phosphonic esters are in the presence of hydroquinone and no reaction when the same esters are placed in contact with glycol acetate?

It has already been remarked in the case of acidolysis that the reaction was less advanced with glycol acetate. In the case of transesterification, another phenomenon intervenes. Hence, while there is no reaction between the phosphonic esters and the glycol acetate at 300°C, there is the beginning of a reaction between the ethyl benzenephosphonate and the butanediol diacetate (table V).

TABLE V SUPPLEMENTARY TESTS AT 300°C						
		Ambient trap	Icewater trap	Liquid nitrogen trap	Residue	Observations
ethyl benzene-phosphonate	1,4-butanediol diacetate	ethyl tetrahydrofuran and acetic acid	ethyl acetate; traces of ethyl alcohol	ethylene	two layers, one liquid, the other solid; the liquid contains acetic acid, small amount of ethyl benzenephosphate and traces of butanediol diacetate	principally esterification, some transesterification
phenyl benzene-phosphonate	1,4-butanediol diacetate	small amount of liquid butanediol acetate and acetic acid	-	propylene or butene	product unaltered	no reaction
ethyl butane-phosphonate	1,4-butanediol diacetate	-	-	ethylene	product unaltered	no reaction

Noting the boiling points of the various reagents present, it turns out that glycol diacetate boils at 190°C and butanediol diacetate at 224° at 760 mm Hg pressure. It is apparent that a mixture of a medium which boils at 190° and a heavier medium immersed in a bath at 300° will never reach this temperature. Consequently, it is likely that in this case the temperature of decomposition of the ethyl phosphonates is not reached.

If hydroquinone acetate, which boils at 370-380° at 760 mm Hg pressure, is used, such decomposition takes place and there is a reaction.

The higher reactivity of the ethyl benzenephosphonate relative to ethyl butanephosphonate could also be explained by the larger volatility of the latter compound.

Following are the boiling points of the two indicated esters:

- Ethyl butanephosphonate: E 1 mm = 74°C.
- Ethyl benzenephosphonate: E 0.3 mm = 100°C.

V. CONCLUSION

The authors are inclined to regard the synthesis of polyphosphonates, both in the alcane series and in the arylphosphonic series, as for the most part extremely difficult. However, such a method has been the subject of a communication by Coover and McCall (ref. 2), who prepared phosphonic polyesters by the action of phenyl esters on diphenols.

Inasmuch as the preparation of polyphosphonates by transesterification presents numerous advantages, an attempt has been made in the present work to examine the various possibilities for this method of synthesis. The following three methods of transesterification have been tested experimentally and discussed: alcoholysis, acidolysis, and transesterification proper.

V.1. Alcoholysis

The diphenyl phosphonates combine with hydroquinone in the presence of magnesium chloride at 200°C to give the exchange reaction described by Coover and McCall. This reaction occurs without the formation of secondary products.

In the presence of hydroquinone, the diethyl phosphonates lead to secondary reactions resulting in the formation of ethers, ethylene, etc. If the hydroquinone is replaced by aliphatic diols, etherification becomes the principle reaction.

V.2. Acidolysis

The acidolysis reaction takes place at 200°C in the presence of magnesium chloride much more readily than alcoholysis, both with hydroquinone diacetate and with glycol diacetate. It is more complete, however, for the hydroquinone diacetate.

The synthesis of polyphosphonates by acidolysis of the carboxylic diesters by butane- and benzenephosphonic acids occurs without the formation of secondary products.

V.3. Transesterification

The preparation of polyphosphonates by this method is more difficult to realize than by alcoholysis or acidolysis. At 200°C the reaction is extremely slow; it is more rapid at 300°.

It does not take place except in the case of the diethyl phosphonates. But the diethyl phosphonates decompose at 300°, giving rise to the phosphonic acids, ethylene, and other secondary products identified in the course of these reactions.

It was demonstrated in various supplementary investigations that transesterification never transpires in the absence of free phosphonic acid.

It is probably that the transesterification between the phosphonic diesters and the carboxylic diesters is a very slow reaction at the temperatures investigated. It almost fails to occur at all, other than in the case when degradation of the phosphonic ester yields phosphonic acid. In this case, acidolysis takes place very readily.

In conclusion, it may be asserted that true transesterification per se never occurs. It is easiest to produce phosphonic polyesters by acidolysis.

In the event that one should wish to prepare a polyester of a diphenol, alcoholysis can be used providing a diphenyl phosphonate is employed. The alcoholysis reaction is slower, all other conditions being equal, than the acidolysis reaction.

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